



Interactions between Eutrophication and Contaminants. II. Mobilization and Bioaccumulation of Hg and Cd from Marine Sediments

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The availability of labile organic matter and oxygen from the bottom water are primary factors most likely to affect the accumulation of contaminants in benthic invertebrates. To test this hypothesis, a two-factor microcosm experiment was designed. Three species of sediment-dwelling organisms were kept in sediments spiked with ^{203}Hg and ^{109}Cd . Blue mussels were kept downstream in separate vessels. Different treatments were obtained by combination of two levels of organic carbon (enriched, not enriched) with two levels of oxygen ($7\text{--}9\text{ mg l}^{-1}$ and $2\text{--}3\text{ mg l}^{-1}$) in the water flowing through the aquaria. After an experimental period of three months, gamma emission from the two isotopes were counted in samples of sediments, porewater and biota. The results showed initial retention of a labile fraction of Cd in the carbon-enriched sediments. Hg was retained to the same extent in all treatments and no significant loss from the sediment was observed during the experimental period. In the porewater, Hg was not detectable whereas the concentration of Cd was consistent with the levels predicted from low sulphide ion activities recorded on $\text{Ag}|\text{Ag}_2\text{S}$ electrodes and the solubility of $\text{CdS}_{(s)}$. Two-way ANOVA analyses revealed significant effects of carbon enrichment on bioaccumulation of both Cd and Hg. Significant effects of oxygen level and oxygen-organic interactions were found for the bioaccumulation of Cd only. © 1997 Elsevier Science Ltd

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During the last decades, the benthic environment of many lakes, estuaries and fjords has been exposed to

enhanced inputs of contaminants (Magnusson *et al.*, 1996) and increased loading of organic matter (Baden *et al.*, 1990; Heip, 1995; Rast and Holland, 1988). Eutrophication related effects, such as increased primary production, increased sedimentation of organic carbon, proliferation of filamentous algae, oxygen deficiency in the bottom water and changes in benthic communities, have been reported in many coastal environments between the southern North Sea and the Baltic (Westernhagen and Dethlefsen, 1983; Josefson and Rosenberg, 1988; Rosenberg *et al.*, 1990; Richardson and Heilmann, 1995).

In the sediments, deposition of fresh organic carbon and the availability of oxygen from the bottom water are primary factors affecting a number of geochemical and biological processes and most likely, the bioaccumulation of contaminants. Therefore, an experiment was designed, using ^{203}Hg and ^{109}Cd to assess the effects of oxygen availability and sediment carbon content on the partitioning of contaminants between sediments, pore water and biota. The two metals are xenobiotic and potentially toxic contaminants with principally different geochemical behaviour. Hg is influenced by atmospheric input, short residence times and rapid scavenging in the deep ocean (Gill and Fitzgerald, 1988), whereas Cd has a characteristic nutrient type distribution with surface depletion, subsurface remobilization and a long residence time (Bruland, 1983; Kremling, 1983, 1985).

Material and Methods

Experimental set-up

The experiment was performed at the Marine Research Station Solbergstrand (MFS) using twelve continuously flushed glass aquaria ($28 \times 46 \times 23\text{ cm}$) within which three sediment-dwelling species (*Abra alba*, *Nereis diversicolor* and *Amphiura filiformis*) were

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kept in a layer of non-contaminated, marine clay sediment. Blue mussels (*Mytilus edulis*), were exposed to the water flowing out of the sediment aquaria. The twelve aquaria used for this experiment was part of a larger set-up described elsewhere in this volume (Skei *et al.*, this volume; Hylland *et al.*, 1997; Gunnarsson *et al.*, 1997).

The source sediment used throughout the experiment had a carbon content of 11 mgC g^{-1} (dry wt) and 80–85% of the particles in the $< 63 \mu\text{m}$ size fraction. Aliquots of source sediment were suspended in seawater and spiked with dissolved chlorides of ^{203}Hg and ^{109}Cd . Thawed aggregates of algae from a batch culture of *Skeletonema costatum* were added to half of the suspensions, which were then allowed to age for two days in the dark, at about 10°C and at constant stirring. After addition to the water in the aquaria, the spiked material was allowed to settle for two days before initiation of the water flow. Seven days later (= day zero) organisms collected in non-polluted locations in the Skagerrak region were transferred to the aquaria.

Seawater was continuously supplied from 60 m depth in the fjord adjacent to the research station. In one branch of the source water the concentration of oxygen was lowered from $7\text{--}9 \text{ mg kg}^{-1}$ (normoxic) to a level of approximately 2 mg kg^{-1} (deoxygenated). Between the main aquaria and the vessels containing the mussels, the water was aerated to restore normal oxygen concentrations in all treatments.

Thus, the factorial set-up using twelve aquaria and two levels (high–low) of each factor (oxygen and algae) yielded three replicate aquaria for each of the four treatments.

Sediment and biota were sampled on day zero and at the termination of the experiment 93 days later. Various observations (S^{2-} , redox-potentials, loss on ignition) performed during the first weeks of the experiment revealed only minor effects of the initial addition of algae. This was later confirmed by analyses of carbon and nitrogen (Fig. 1). Therefore, on day 60, during a 12-h stop of the water flow, a second dose corresponding to 20 gC m^{-2} was added to the enriched aquaria by mixing aliquots of thawed aggregates of *S. costatum* into the overlying water.

Sampling and analytical methods

The water quality was monitored by daily or more frequent recordings of temperature, salinity and oxygen using standard, commercially available sensors. Redox potentials (E_h) were measured on a Pt-electrode inserted to a sediment depth of 1 cm.

Sulphide ion activities were recorded on $\text{Ag}|\text{Ag}_2\text{S}$ electrodes permanently positioned in the overlying water and at 1-cm depth intervals down to a sediment depth of 4 cm. This was accomplished by mounting six sulphide coated silver bars (2 mm wide) at 10-mm (cc) intervals on a PVC-rod. Nine rods were permanently positioned across the sediment–water interface in 2(3)

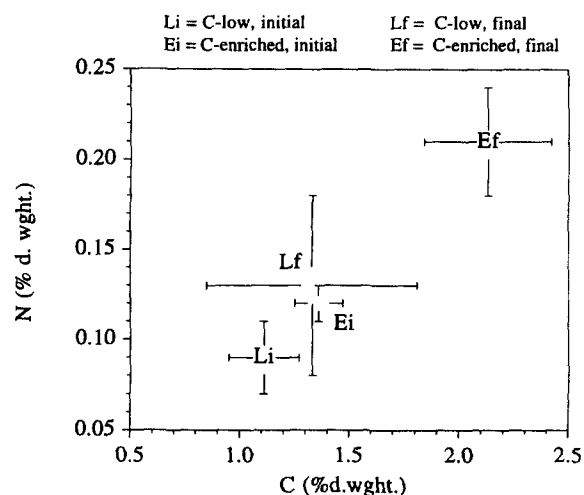


Fig. 1 Plot of initial (i) and final (f) concentrations of carbon vs nitrogen in 0–1 cm depth interval in carbon-enriched (E) and carbon-low (L) aquaria. Each point is the mean value of six aquaria. Error bars = \pm one std. dev.

aquaria from each treatment. Electrode potentials were recorded continuously against an $\text{Ag}|\text{AgCl}$ reference electrode, using a 60-channel data logger.

Sediment samples were collected using a cut-off 13 mm (ID) PVC-syringe. Five cores were drawn from each chamber. One centimetre sections were cut off and pooled in the centrifuge tubes used for separation of the pore water at $20\,000 \text{ g}$ for 15 min. Centrifugation was completed less than 12 h after the cores had been removed from the aquaria.

Immediately after the final sampling of the sediment, organisms were carefully transferred to beakers with seawater (*N. diversicolor* and *A. filiformis*) or clean sediment (*A. alba*). After defecation, the sediment-dwelling species were divided into 1–7 pools from each aquarium. Each pool was homogenized in a glass/teflon homogenizer before subsampling for tracer analyses. The soft tissues of the mussels were removed after drop drying and tracer analyses were performed on individual animals.

All analyses for ^{109}Cd and ^{203}Hg were done at the Institute for Energy and Technology (IFE), using a $\text{Ge}(\text{Li})$ gamma spectrometer for the sediment samples, a low level HPGe-gamma spectrometer for the biological samples or a Quantulus low level liquid scintillation spectrometer for the pore water and some of the biological samples. All results were corrected to day zero activities according to the half-lives of 46.6 days for ^{203}Hg and 453 days for ^{109}Cd .

Calculation of pS and $\Sigma[H_2S]$

Activities of S^{2-} sulphide ions in the pore water are directly proportional to the electrode-potentials:

$$-\log \{ \text{S}^{2-} \} = (E_{\text{obs}} + E_{\text{ref}} + E_0') / 0.0295 \quad (1)$$

in which

- E_{obs} = recorded cell potential
 E_{ref} = potential of the reference electrode at ambient temperature
 E_0' = standard potential of Ag|Ag₂S electrode at ambient temperature and salinity
0.0295 = Nernst equation constant for two-electron transfer at 25°C.

The total concentration of hydrogen sulphide can be calculated from the equation:

$$pS' = -\log(\Sigma[H_2S]) = -pK_2 + pH - \log\{S^{2-}\} - \log(10^{(pK_1-pH)} + 2.22) \tag{2}$$

which is valid at $pH \leq 10$. K_1 and K_2 are the first and second dissociation constant for H_2S . The following values: $pK_1 = 13.9$, $pK_2 = 7.0$, $E_{\text{ref}} = 0.2314$ V, $E_0' = 0.6689$ V and $pH = 7.8$ was used throughout the calculations (Boulegue, 1978; Millero *et al.*, 1988). In well-oxygenated environments the potential may drift to yield very high pS. For all data on pS reported below, extreme values were smoothed according to the logical relation: If $pS' > 14$, $pS = 14 + (pS' - 14)/10$, else $pS = pS'$.

Statistical analyses

Data were analysed using two-way analyses of variance (ANOVA) with C-enrichment and oxygen level as the two factors. Nested analyses were applied on the biological data for which up to seven samples from each experimental unit (aquarium) had been analysed. Data were checked for normality (Shapiro-Wilk) and log-transformation were applied when necessary.

Results

Experimental environment

The experimental environment was primarily controlled by the natural variations in the supplied seawater. Temperature varied between 6.1 and 10.1°C and the salinity was 33.6–34.6 PSU. Illumination of the experimental hall oscillated between 12 h darkness and 12 h weak daylight. Bright light was only allowed during sampling and inspection.

Oxygen was recorded daily at the outlet from all aquaria. At a few occasions, concentrations in the deoxygenated aquaria exceeded 4 mg l⁻¹, but the low level was immediately restored by adjustment of the N₂-purging system. For the experimental period, the mean concentrations ranged 2.4–3.6 mg l⁻¹ in the deoxygenated and 7.0–7.3 mg l⁻¹ in the normoxic aquaria. The minimum concentrations ranged 0.6–1.5 mg l⁻¹ in the deoxygenated and 5.7–6.0 mg l⁻¹, in the normoxic aquaria (Skei *et al.*, this volume).

Redox-potentials recorded at 1 cm depth on day 46 ranged 180–352 mV. Loss on ignition (5 h, 450°C) determined in C-enriched and C-low aquaria on day 55 was 45.9±5.2 and 43.4±6.2 mg g⁻¹, respectively. This

lack of significant difference between the C-enriched and the C-low treatments became clear during the experiment and led to the addition of the second dose of algae. Analyses performed after the termination of the experiment, confirmed that also on day zero, the effect of the initial algae addition on the levels of carbon and nitrogen had been rather small compared to the effect of the second dose (Fig. 1). According to the classification system used for Norwegian coastal sediments (Rygg and Th  lin, 1993), only the final concentrations of organic C and N in the C-enriched treatments (E_r in Fig. 1) exceeded the upper limit set for a non-polluted environment. Thus, with regard to organic enrichment, the experimental environment could be classified as non-polluted to moderately polluted. Final concentrations of carbon and nitrogen in the sediment had not been affected by different levels of oxygen.

Due to long stabilization times for the electrode potentials and some initial delay, data for the first 12 days of the experimental period have been omitted. For the remaining 12–93-day period, potentials on each sensor were recorded continuously and integrated values were stored on the logger every 12 h. The maximum concentration of hydrogen sulphide ($\Sigma[H_2S]$) was 10^{-8.54} M (Table 1, pS=8.54). This maximum was recorded on day 36, in one of the oligotrophic (low-C, high-O₂) aquaria, at a sensor located below the spiked layer (4 cm depth). As shown in Table 1, the variation on each electrode (0.98≤std. dev.≤1.66 at 2 cm depth) was large compared to the difference in minimum pS between treatments. Thus, with regard to maximum $\Sigma[H_2S]$, no significant difference was observed between treatments. However, the mean values were different and revealed several expected features such as the decrease of pS at 2 cm depth from 13.37 in the most oligotrophic treatment to 10.29 in the most eutrophic treatment (Table 1) and lower pS within the C-enriched layers than at corresponding depths in the C-low aquaria (Fig. 2). Furthermore, reduced penetration of oxygen may explain the displacement of the pS-cline towards the sediment-surface in the deoxygenated aquaria (Fig. 2).

The low (nanomolar and less) level of H₂S was also confirmed by the high redox potentials measured at

TABLE 1

Minimum and mean pS in various treatments for the 12–93 days recording period. Std. dev.=one standard deviation, n=number of readings. HL=normoxic, low-carbon (oligotrophic), LL=deoxygenated, low-carbon, HH=normoxic, carbon-enriched, LH=deoxygenated, carbon-enriched (eutrophic).

	HL	LL	HH	LH
Minimum pS (all depths)	8.54	8.67	8.91	8.75
Minimum pS (2 cm)	10.03	9.16	9.63	9.14
Mean pS (2 cm)	13.37	11.16	12.35	10.29
Std. dev. (2 cm)	1.63	1.66	1.43	0.98
n(2 cm)	360	360	360	540

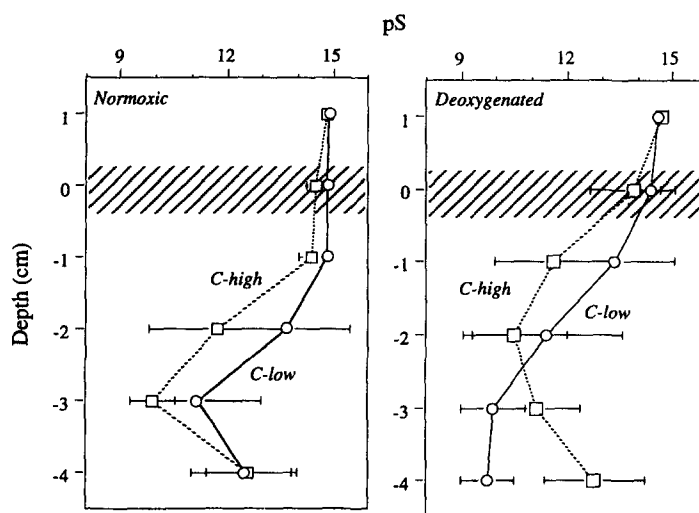


Fig. 2 Profiles of pS across the sediment-water interface during the 12-93-day period (continuously recorded on Ag/Ag₂S electrodes, error bars = ± 1 std. dev. ($n = 360$ 12 h integrated readings)).

1 cm depth on day 46 ($180 \text{ mV} \leq E_h \leq 352 \text{ mV}$, duplicate measurements in all aquaria). Thus, it could be concluded that severe sulphide events did not occur in any of the aquaria and that the electrodes appeared suitable for monitoring pS at concentration levels in the sediments which on the basis of smell and colour, would be referred to as oxic or non-sulphidic.

Sediment and pore water

In all samples of the pore water, the concentration of Hg ([Hg]) was below the limit of detection. In the sediment [Hg] decreased from maximum values in the spiked surface layer to low levels in the non-contaminated layer below 2 cm depth (Fig. 3c). The initial [Hg] of $158 \pm 11 \text{ Bq g}^{-1}$ dry sediment (0–1 cm, ± 1 std. dev., $n = 12$), was not significantly different from the final [Hg] of $170 \pm 23 \text{ Bq g}^{-1}$, and no significant difference was found between treatments (Figs 3c and 4b, Table 2). Thus, the profiles gave no evidence for the presence of any processes acting to redistribute the initially retained Hg. The mean [Hg] of 164 Bq g^{-1} (0–1 cm, all treatments, initial and final) corresponded to $1.14 \text{ nmolHg g}^{-1}$ (dry wt) which has been classified as a 'moderately polluted' coastal sediment (Rygg and Th  lin, 1993).

At the start of the experiment the [Cd] of $1026 \pm 67 \text{ Bq g}^{-1}$ in the C-enriched aquaria was significantly higher than the [Cd] of $874 \pm 45 \text{ Bq g}^{-1}$ in the C-low treatments (Figs 3 and 4a, Table 2). During the experimental period, [Cd] decreased in all treatments, but in the final samples no significant ($p > 0.35$) difference were found between any of the four treatments. Thus, the loss of Cd had been larger in the C-enriched than in the C-low aquaria. The mean [Cd] of $824 \pm 154 \text{ Bq g}^{-1}$ (0–1 cm, all treatments, initial and final) corresponded to $41.0 \text{ nmol Cd g}^{-1}$ (dry wt),

which has been classified as a 'markedly polluted' coastal sediment (Rygg and Th  lin, 1993).

In the pore water, [Cd] ranged between 12.1 and 17.2 Bq g^{-1} (603–857 nM) in the oligotrophic treatment, which was high compared to 2.9–6.8 Bq g^{-1} (145–339 nM) in the other aquaria (Fig. 3b). In the pore water, both deoxygenation ($p < 0.0001$) and algae addition ($p = 0.0009$) had significant effects in lowering [Cd].

At depths below 1 cm, neither Cd nor Hg showed any significant difference between treatments and [Cd] in pore water was close to the limits of detection. The linear profiles of [Hg] (Fig. 3c), showed that the final samples from the 1–2 cm depth interval represented a mixture of 50% of the spiked surface layer and 50% of the non-contaminated base sediment. The fact that the final [Cd] at 1–2 cm depth, corresponded to 50% of the initially retained [Cd] in the surface layer (Fig. 3a) showed that significant loss of Cd was restricted to the 0–1 cm layer. Neither did the vertical profiles of [Cd] in pore water (Fig. 3b) reveal any distortion of the concavity expected from a source situated within the 0–1 cm layer. (The profile in the most eutrophic treatment was slightly different and may have resulted from increased precipitation of $\text{CdS}_{(s)}$ within the 0–1 cm layer after the second addition of algae.) Thus, neither sediments nor pore water samples gave any evidence for mobilization of Cd from depths exceeding 1 cm in any treatment.

Biota

In *A. alba* no difference was found between the [Cd] in normoxic and deoxygenated treatments at the same C-levels. Between C-levels, however, a large difference from 93–134 Bq g^{-1} (wet wt) in the C-low aquaria to 741–795 Bq g^{-1} in the C-enriched aquaria was ob-

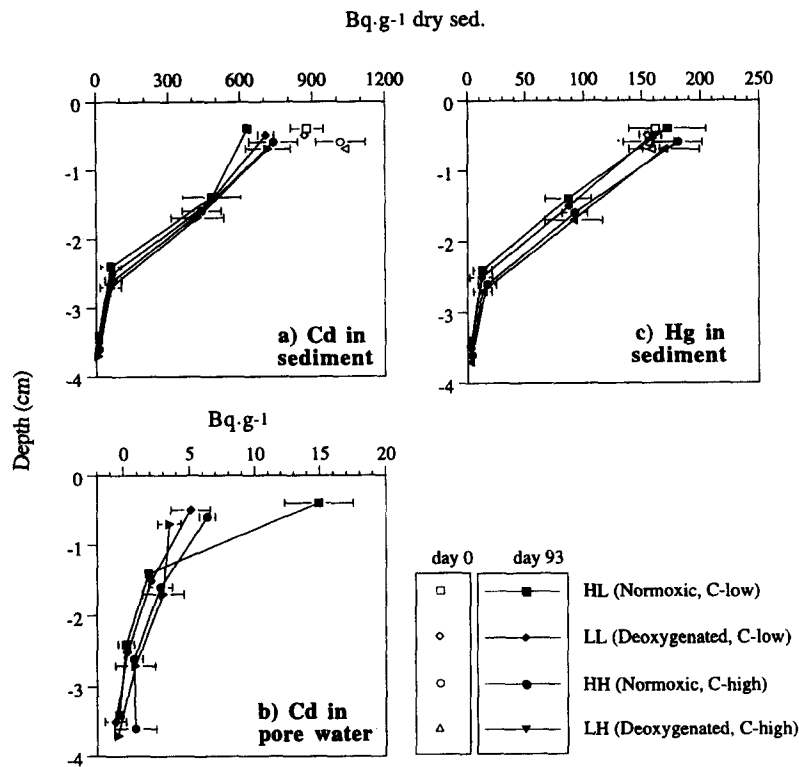


Fig. 3 Vertical profiles of mean activities of ^{109}Cd and ^{203}Hg in sediments and pore water on day 0 (0–1 cm, open symbols) and 93 (profiles, filled symbols). Error bars = ± 1 std. dev. ($n=3$ replicate aquaria). Note: vertical separation of symbols does not affect shape of profiles.

TABLE 2

Analyses of variance (ANOVA) on the effects of oxygen level, organic addition and oxygen/organic interactions on the activities of ^{109}Cd and ^{203}Hg in sediment, pore water and biota. R^2 = fraction of total variance explained by the model, n = number of analyses and p = probability.

	R^2	n	p		
			Oxygen	Organic	Interactions
Cd					
Sediment, initial	0.69	12	0.92	0.003	0.72
Sediment, final	0.32	12	0.54	0.20	0.26
Pore water	0.92	12	<0.0001	0.001	0.08
<i>M. edulis</i>	0.13	37	0.01	0.10	0.003
<i>Abra alba</i>	0.81	12	0.95	0.0001	0.66
<i>Nereis diversicolor</i>	0.02	36	0.20	0.05	0.20
<i>Amphiura filiformis</i>	0.20	35	0.05	0.18	0.01
Hg					
Sediment, initial	0.06	12	0.75	0.82	0.56
Sediment, final	0.12	12	0.43	0.55	0.99
<i>Abra alba</i>	0.87	12	0.47	<0.0001	0.38
<i>Nereis diversicolor</i>	0.14	36	0.53	0.003	0.33
<i>Amphiura filiformis</i>	0.24	35	0.95	0.06	0.14

served (Fig. 4a). The ANOVA analyses (Table 2) showed that the organic factor could account for a major part of the variance between treatments, whereas the oxygen factor was not important. In *M. edulis* and the two sediment-dwelling species, *N. diversicolor* and *A. filiformis*, the [Cd] ranged between 4.0 and 20.9 Bq g⁻¹. In the mussel, the highest [Cd] was

observed in the oligotrophic treatment and significant interactions between the organic and oxygen factors showed that increased uptake of Cd from the normoxic aquaria was dependent on low organic level. In *N. diversicolor* and *A. filiformis*, however, the highest [Cd] occurred in the most growth-promoting environment (Hylland *et al.*, 1997) with high oxygen level and algae

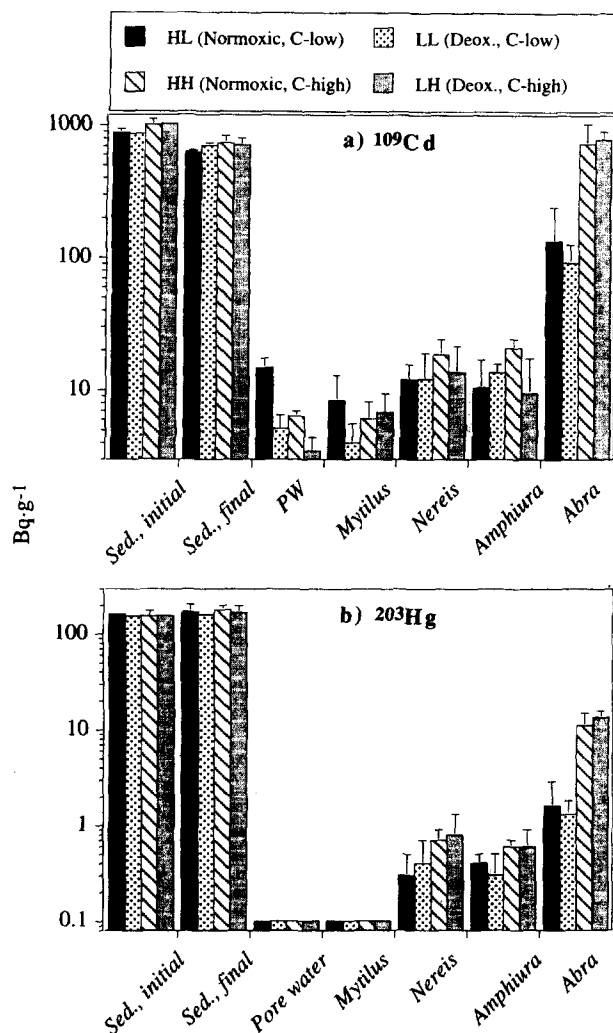


Fig. 4 Activities of ^{203}Hg and ^{109}Cd in sediment (0–1 cm), pore water and biota. Units (Bq g^{-1}) were normalized against sediment dry wt and biota wet wt. Error bars = 1 std. dev.

added. The organic factor had significant effects on [Cd] in *N. diversicolor* ($p=0.05$), whereas interaction effects in *A. filiformis* ($p=0.006$) showed that the accumulation of Cd in the C-enriched treatments was dependent on oxygen availability.

[Hg] was below detection limits in all samples of *M. edulis*. In *N. diversicolor* and *A. filiformis* [Hg] ranged between 0.3 and 0.8 Bq g^{-1} . In *A. alba* [Hg] ranged 1.3–1.6 Bq g^{-1} in the C-low treatments and 11.1–13.5 Bq g^{-1} in the C-enriched treatments. Addition of algae seemed to affect [Hg] in all sediment-dwelling species ($p \leq 0.06$) whereas the oxygen factor was not significant ($p \geq 0.47$).

The increase of the $^{109}\text{Cd}:^{203}\text{Hg}$ activity ratio (Fig. 5) from 3.7–4.3 in the sediment to 18.2–51.8 in *N. diversicolor* and *A. filiformis* and as high as 60.2–74.9 in *A. alba*, showed strong preferential accumulation of Cd in the three sediment-dwelling species. The simultaneous decrease of the $^{109}\text{Cd}:^{203}\text{Hg}$ activity ratio in the sediment (Fig. 5) and the negligible change in [Hg] (Fig. 4b), were consistent with the initial presence

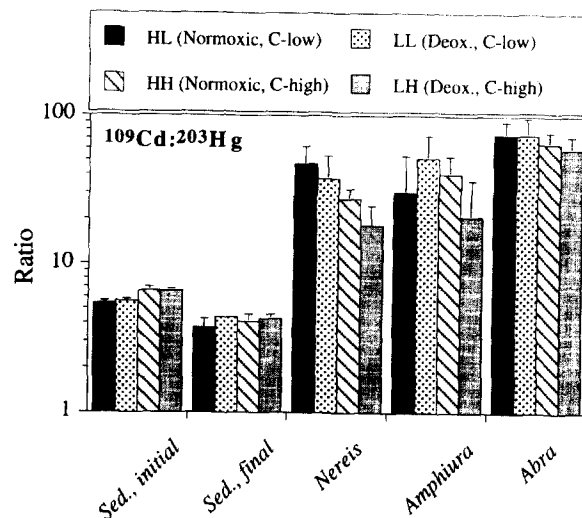


Fig. 5 ^{203}Hg and ^{109}Cd activity ratios in sediment (0–1 cm), pore water and biota.

of labile, bioavailable Cd in the sediment in all treatments.

Discussion

Partitioning of Hg and Cd

Contaminant levels in the sediment were within the range of concentrations frequently found in moderately polluted areas, and the concentration of H_2S remained low throughout the experimental period in all treatments. No negative effects on metabolism (biomarkers, growth parameters) were observed (Hylland *et al.*, 1997). Thus, experimental bias on observed bioaccumulation patterns caused by toxicity of contaminants or hydrogen sulphide, was probably not involved.

The observed retention of excess [Cd] in sediments treated with *S. costatum* (Fig. 3a), as well as the preferential uptake of Cd (relative to Hg) in all of the sediment-dwelling species (Fig. 5), was consistent with the frequently reported affinity of Cd to dead and living organisms (Collier and Edmond, 1983, 1984; Golimowski *et al.*, 1990). *Abra alba* is known to feed selectively on food items which is picked up by rapid and precise movements of the siphon. In the present experiment, *A. alba* was found to grow more rapidly than the other species (Hylland *et al.*, 1997), and efficient feeding on the Cd-contaminated algae appeared to be the primary pathway explaining the 100× higher [Cd] in this organism as compared to the other species. Collier and Edmond (1983) showed that the Cd associated with planktonic matter from sediment traps was easily desorbed. Consistently, the excess phase of Cd present on day zero disappeared during the experimental period. Thus, the present experiment indicated that Cd adsorbed on the dead algae represented a highly available source of Cd for organisms feeding on the detritus.

The absence of detectable amounts of Hg both in pore water and *M. edulis* indicated that uptake of Hg via the pore water pathway was not important. The retention of Hg in sediments treated with algae was not different from the retention in the other sediments (Fig. 3c, 4b). Nevertheless, [Hg] had increased in all sediment-dwelling species exposed to algae-enriched sediments. Again the effect was most strongly pronounced in *A. alba*, which showed 10× higher [Hg] than the other species. It appears that feeding behaviour had affected metal uptake even when the metal was not associated with the principal food item. If, however, increased feeding in the algae-enriched sediments had been accompanied by increased ingestion of Hg-contaminated sediment, and some of this Hg was retained in the organisms, bioaccumulation should be stronger in the C-enriched than in the C-low sediments, as observed.

The oxygen factor had no significant effect on bioaccumulation of Hg, but was relevant for the bioaccumulation of Cd (Table 2). In *M. edulis* exposed to Cd in dissolved and particulate phases flowing through the downstream aquaria, the highest concentration in the oligotrophic treatment was consistent with the high [Cd] in the pore water of the corresponding treatment (Fig. 4a). This showed that leakage via the pore water may have accounted for a significant fraction of the total loss Cd from the sediments. Significant interactions between the oxygen and organic factor (Table 2) had, however, resulted in high [Cd] in the most eutrophic treatment in spite of low [Cd] in the pore water. Mechanisms such as increased bioturbative resuspension or secretions from more actively feeding organisms, may have been involved to account for the relatively high [Cd] and significant interaction effects in the mussels located downstream of the C-enriched sediment.

The two sediment-dwelling species *N. diversicolor* and *A. filiformis* might be more dependent on pore water quality than *A. alba*, which has a protective shell and can feed and respire through its siphon on the sediment surface. This was confirmed by the ANOVA-analyses which showed lower *p*-values for interaction effects in *N. diversicolor* and *A. filiformis* ($p \leq 0.2$) than in *A. alba* ($p = 0.66$). Significant interactions were, however, only found for *A. filiformis* ($p = 0.006$). *Nereis diversicolor* is known to be tolerant to hypoxia (Schöttler, 1979; Vismann, 1990) and in several experiments performed at MFS, *N. diversicolor* has been observed to survive severe sulphide events in the pore water without leaving their burrows within the sediment. *Amphiura filiformis*, is known to be more sensitive to hypoxia and may respond to low oxygen by escaping from their normal location inside the sediment (Rosenberg *et al.*, 1991; Diaz and Rosenberg, 1995; Nilsson and Sköld, 1996). In the present experiment, sulphide concentrations were not severe and both species remained buried in the sediments. However, only *A. filiformis* showed a significant effect from the oxygen factor. If the

accumulation of Cd in *A. filiformis* in the normoxic aquaria was stimulated by the higher [Cd] in the pore water, it appears that *A. filiformis* is more exposed to the pore water environment than *N. diversicolor*. Thus, the observed bioaccumulation patterns in the two species were consistent with the different behaviour shown by the two species when exposed to hypoxia.

Low level sulphide solubility control?

Because the Ag|Ag₂S electrode selectively measures the activity of S²⁻ ions, the potentials recorded on such electrodes should be ideal for sulphide solubility calculations. Within the sediment surface, characteristic pS-values ranged between 10 and 14 (Table 1) corresponding to recorded potentials (*E*_{obs}) between –296 and –415 mV. Solving Eq. 1 for this range of potentials gave activities of S²⁻ between 10^{–16.5} and 10^{–20.5} M. The mean activities of ¹⁰⁹Cd in the pore water of the four treatments ranged between 3.5–14.9 Bq g^{–1}. Using the specific activity of 0.0056 µgCd.Bq^{–1}, an activity coefficient of 0.2 for the divalent ion (Debye and Hückel, 1923) and disregarding Cd-complex formation, activities of Cd²⁺ of 10^{–6.8}–10^{–7.5} M were calculated. By multiplication of the highest activities of Cd²⁺ with the lowest activities of S²⁻ and vice versa, the CdS ion activity product ($\{Cd^{2+}\} \{S^{2-}\}$) within the surface layer ranged from 10^{–24.0}–10^{–27.3}, which was in reasonably good agreement with the solubility product of 10^{–27.0} (Stumm and Morgan, 1981). This gave credibility to the potentials recorded, as well as indicating that Cd in the pore water was controlled by hydrogen sulphide, even at the very low concentrations present in this sediment. If sulphide solubility also controlled [Hg], the solubility product of 10^{–52.7} for HgS would predict non-detectable [Hg] in the pore water, as observed.

It appears that low level sulphide solubility control could explain the complete absence of significant effects of oxygen on bioaccumulation of Hg. The solubility of HgS_(s) is so low that even in the most oligotrophic treatment, Hg was maintained below detection limits. If sulphide solubility was also the primary factor controlling [Cd] in pore water, the activity of sulphate-reducing bacteria yielding low levels of hydrogen sulphide in the apparently non-sulphidic environment, appeared to be responsible for the observed oxygen–organic interaction effects that affected bioaccumulation patterns in *M. edulis*, *A. filiformis* and, to a lesser extent, in *N. diversicolor*. Only in *A. alba* did bioaccumulation of Cd appear to be independent of the sulphide ion activities.

Conclusions

The conclusions from the present experiment are summarized in Fig. 6. In the pore water, the concentration of both metals was consistent with the solubility of the metal-sulphides, even at extremely low

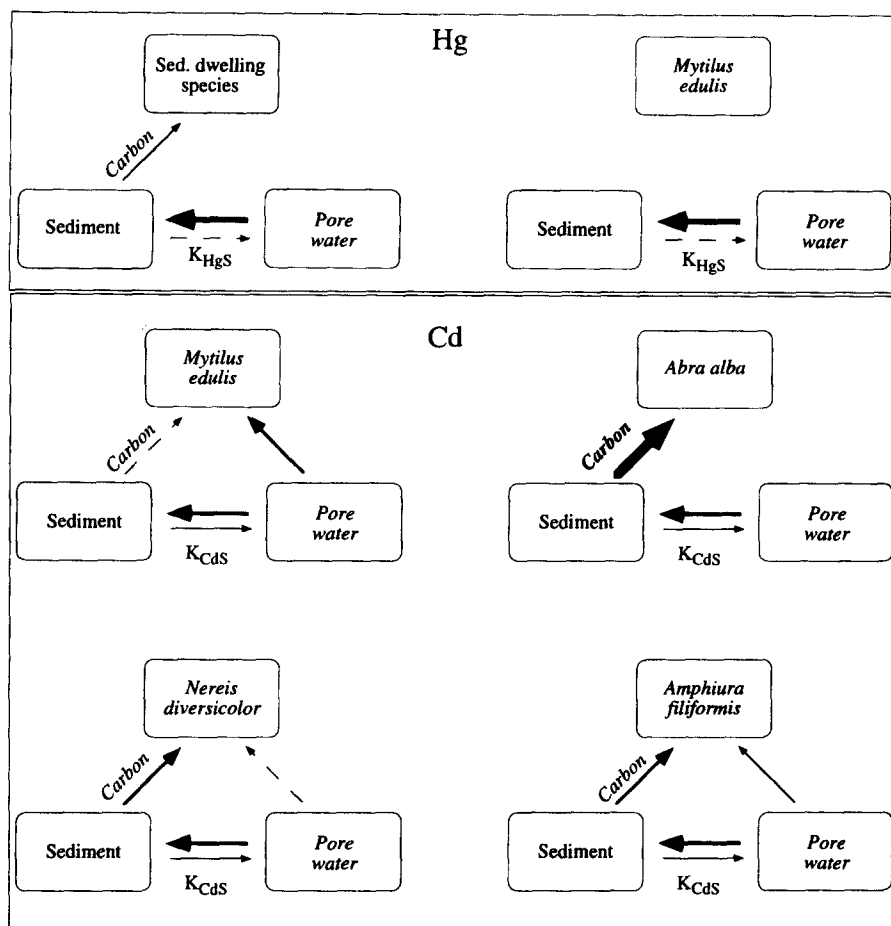


Fig. 6 Relative importance of various pathways of ^{203}Hg and ^{109}Cd from spiked sediment to organism.

concentrations of hydrogen sulphide. Because of the much lower solubility of $\text{HgS}_{(\text{s})}$ as compared to $\text{CdS}_{(\text{s})}$, the concentration of Hg was below detection limits in the pore water. Thus, the bioaccumulation of Hg was controlled by ingestion of sediment particles and significantly stimulated by carbon enrichment. Also, the bioaccumulation of Cd was primarily stimulated by the C-enrichment. Particularly high concentrations in *A. alba* were assumed to result from efficient feeding on algae onto which Cd had been adsorbed. However, significant interaction effects showed that the oxygen level had also affected accumulation of Cd in *A. filiformis* and *M. edulis*. The effects of oxygen on the sediment-dwelling species appeared primarily to occur via effects on hydrogen sulphide and $\text{CdS}_{(\text{s})}$ solubility control of [Cd] in the pore water. The higher oxygen sensitivity of *A. filiformis* indicated that this organism is more exposed to the pore water environment than *N. diversicolor* as long as both remain buried in the sediment.

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